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Contribution from the Department of Chemistry,
Southern University, Baton Rouge, Louisiana

A STUDY OF THE REACTION OF COPPER(II) ION WITH 4-METHYL-3-PENTEN-2-ONE

By Ivory V. Nelson and James Dillon

A spectrophotometric study of the reaction between copper(II) ion and 4-methyl-3-penten-2-one demonstrated that the complex ion, $\text{Cu}(4\text{-methyl-3-penten-2-one})^+$, and the precipitate involving two moles of 4-methyl-3-penten-2-one and one mole of copper(II) ion were formed. The rate of the formation of the complex ion was found to be first order in copper(II) ion, and the reaction to form both the complex ion and the precipitate proceeds at a faster rate in solvents of lower dielectric constant.

Introduction

In a recent study¹ of the polarographic behavior of copper(II) ion

(1) I.V. Nelson, R.C. Larson, and R.T. Iwamoto, J. Inorg. Nucl. Chem., 22, 279(1962).

in 4-methyl-3-penten-2-one, commonly known as mesityl oxide, it was observed that the reduction of copper(II) occurs reversibly only when solutions are heated or allowed to stand for approximately six days. Assuming that this reversibility is due to the formation of a complex consisting of copper(II) ion and the mesityl oxide molecule, a study of the nature and stoichiometry of this reaction should give some insight into the makeup of the electroactive species. This paper reports the result of this study. During the course of this investigation it was observed that the reaction in question proceeded at a rate too fast to study by spectrophotometric means in pure mesityl oxide, thus this study was carried out in acetonitrile, methanol, dimethylsulfoxide, and dioxane.

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Experimental Section

Apparatus. - Absorbance measurements were made with a Beckman DB recording spectrophotometer and matched 1.00-cm silica cells. The temperature was maintained at $23.0 \pm 0.2^\circ\text{C}$ by using jacketed cells in conjunction with a thermostatically controlled water-bath.

Materials. - The organic solvents were purified by treatment with appropriate reagents and fractional distillation^{2,3}. Acetonitrile was fractionally distilled

(2). A.W. Weissberger and E.S. Poskauer, "Organic Solvents", (2nd Ed) Interscience, New York (1955).

(3). A.I. Vogel, "Practical Organic Chemistry", (3rd Ed) Longmans, London, (1956).

from phosphorus pentoxide. Absolute methanol was treated with magnesium activated with iodine and fractionally distilled. Technical grade mesityl oxide was dried with anhydrous potassium carbonate and fractionally distilled after filtration from the potassium carbonate. Dioxane was dried over sodium metal and fractionally distilled. Analytical grade dimethylsulfoxide was fractionally distilled.

Anhydrous lithium perchlorate and copper(II) perchlorate hexahydrate (G.F. Smith Chemical Company) were dried in a vacuum oven at 60°C and used without any further pretreatment. Copper(II) solutions were standardized electrolytically.

Procedure. - To study the rate, a calibration curve for copper(II) was prepared at 740 millimicrons. Aliquots of a 0.2224 M standard solution of copper(II) were added to a 25-ml volumetric flask containing mesityl oxide in acetonitrile, methanol, dimethylsulfoxide, and dioxane. Determinations were made on solutions containing molar ratios of mesityl oxide to copper(II) from 19/1 to 100/1. Absorbance measurements were taken at two minute intervals at 740 millimicrons.

Analysis. - The white precipitate from acetonitrile and dioxane solutions was dissolved in acetonitrile by heating. A small amount of powdered activated charcoal was added and the mixture was heated a few additional minutes. After filtration, the colorless liquid was cooled in an ice bath and long needle-shaped crystals were collected. The copper content was determined electrolytically. Test for the perchlorate anion indicated only trace amounts.

Results

Application of the method of continuous variations⁴ to the system

(4). W.C. Vosburgh and G.R. Cooper, J. Am. Chem. Soc., 63, 437 (1941)

copper(II)-mesityl oxide in acetonitrile demonstrated that one mole of copper(II) ion and one mole of mesityl oxide are involved in the formation of a red colored complex. Figure 1 shows plots of absorbance versus the mole fraction of copper(II) at a wavelength of 740 millimicrons for solutions in which the sum of the concentrations of copper(II) and mesityl oxide are constant. The results were obtained with total concentrations of 0.01 M and 0.0075 M respectively. (Copper(II) plus mesityl oxide). In each case the maximum occurred at a mole fraction of 0.5, indicating the formation of a 1 : 1 complex. Figure 2 shows the spectra of the complex in acetonitrile and pure mesityl oxide.

Further evidence for the existence of a 1 : 1 complex was the constancy of the quantity $A/[\text{Cu}^{++}][\text{Mesityl Oxide}]$ at various concentrations of added copper(II) and mesityl oxide as shown in Table I.

Table I

Values of $A/[\text{Cu}^{++}][\text{Mesityl Oxide}]$		Absorbance	$\frac{A}{[\text{Cu}^{++}][\text{Mesityl Oxide}]}$
$[\text{Cu}^{++}]$	$[\text{Mesityl Oxide}]$		
0.001	0.009	0.27	3.0×10^4
0.002	0.008	0.39	2.5×10^4
0.003	0.007	0.63	3.0×10^4
0.004	0.006	0.71	3.0×10^4
0.005	0.005	0.89	3.4×10^4
0.006	0.004	0.72	3.0×10^4
0.007	0.003	0.63	3.0×10^4

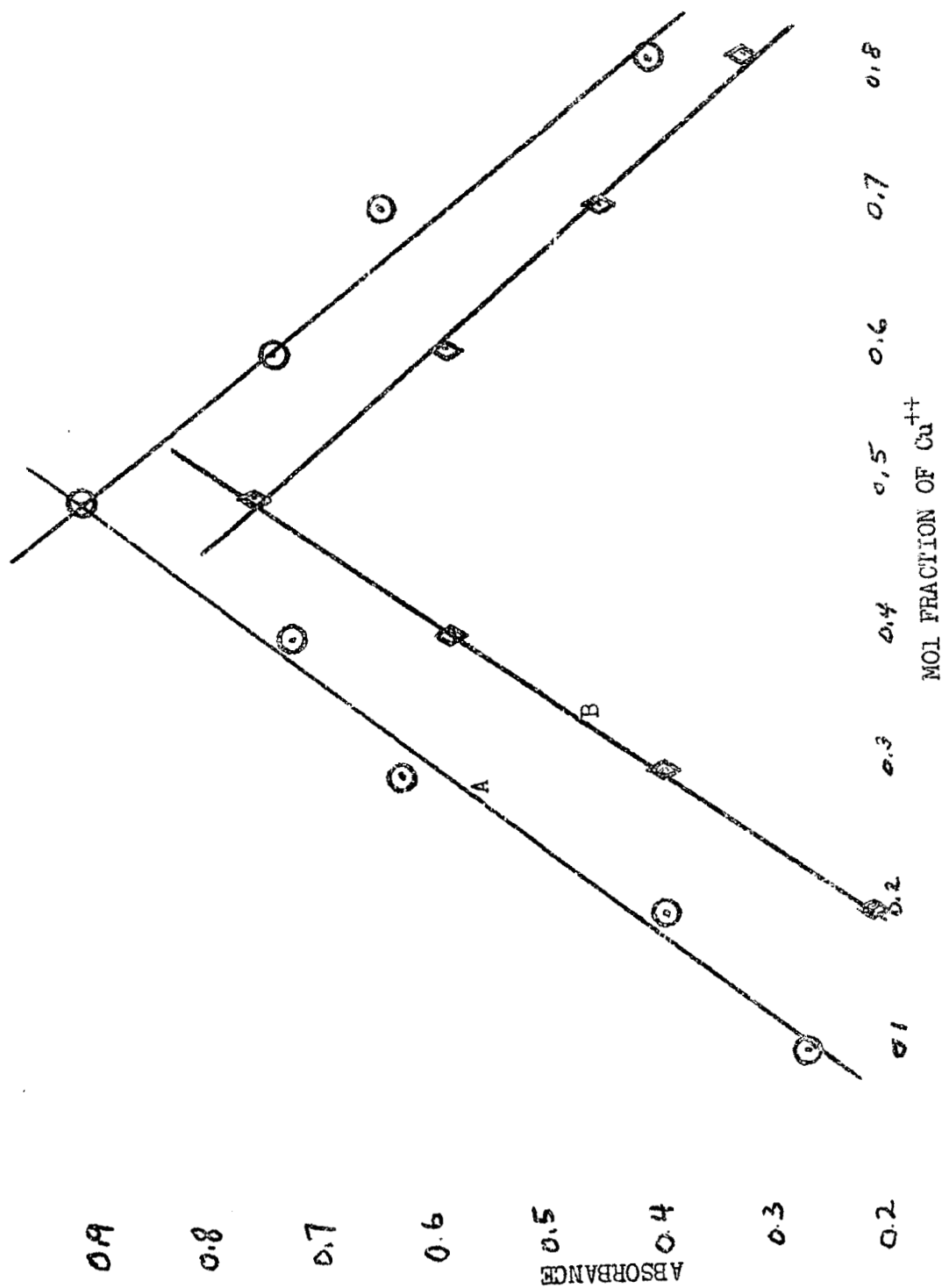


Figure 1--Stoichiometry of the reaction between copper(II) ion and mesityl oxide.
 A. Total concentrations 0.01 M. B. Total concentrations 0.0075 M.

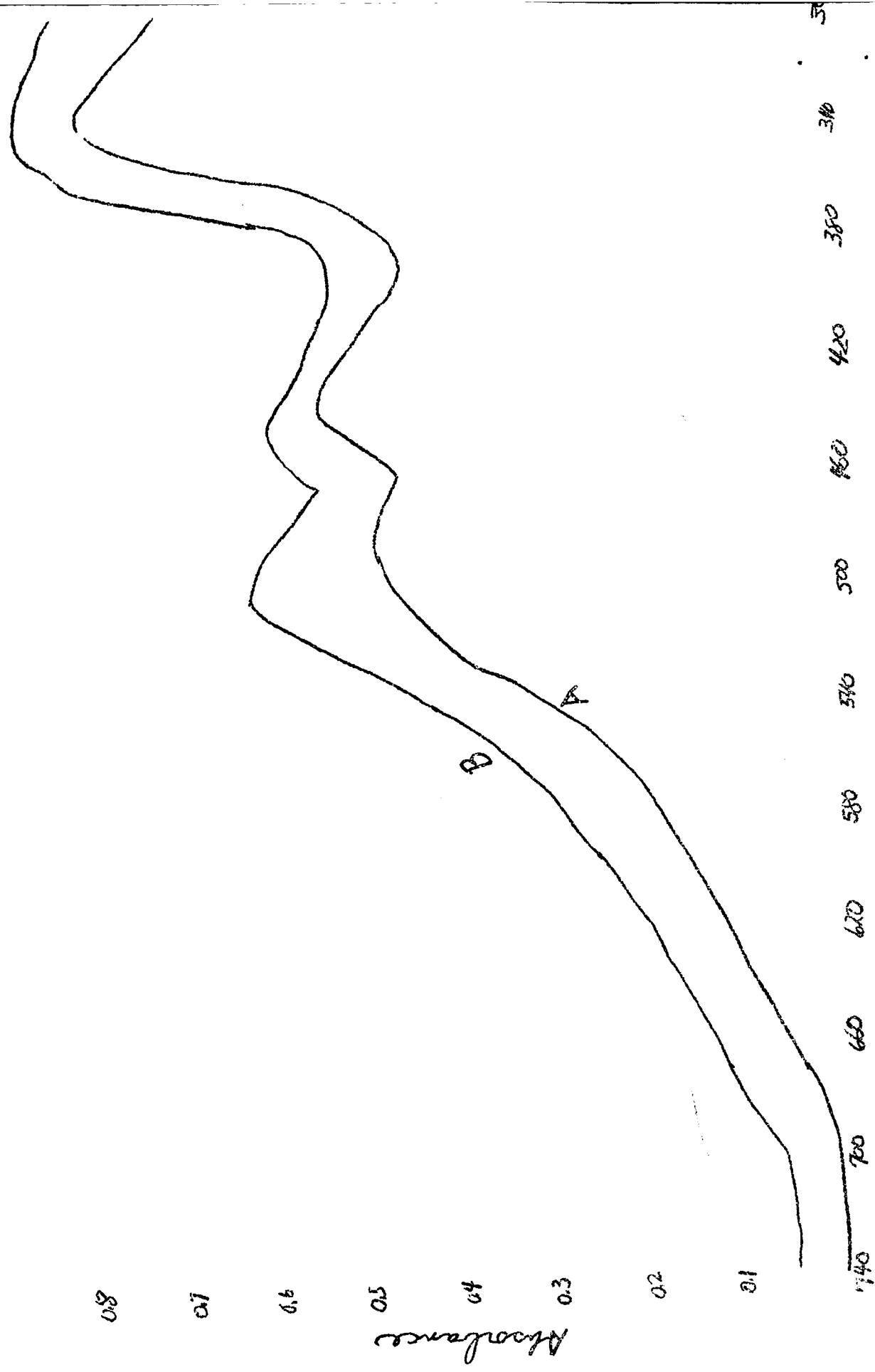


Figure 2.---Visible spectra of $\text{Cu}(\text{Mesityl Oxide})^+$. (A) Acetonitrile (B) Mesityl Oxide

The constancy of this quantity shows that no significant amount of free copper(II) ion exist in the presence of mesityl oxide in these measurements. The values are seen to be constant within experimental error as would be expected for the proposed reaction.

Investigation of the Rate of the Reaction. -- The rate of the reaction of copper(II) ion with mesityl oxide was shown to be first order in copper(II) ion within the molar ratio of mesityl oxide to copper(II) ion from 19/1 to 100/1. Figure 3 shows plots of the logarithm of copper(II) ion concentration versus time. The rate constants for the formation of the copper(II)-mesityl oxide complex are given in Table II.

Table II^a

Rate Constants for the Reaction of
Copper(II) Ion with Mesityl Oxide
to Form Cu(Mesityl Oxide)⁺

$[\text{Mesityl Oxide}] / [\text{Cu}^{++}]$	K	
9/1	4.8×10^{-5}	sec ⁻¹
19/1	1.2×10^{-4}	sec ⁻¹
66/1	4.4×10^{-3}	sec ⁻¹
100/1	2.4×10^{-2}	sec ⁻¹

a

Average of at least three determinations

It was observed that after a few minutes a white crystalline solid appeared in the colored solution. Analysis of this crystalline solid yielded an average copper content as determined from five samples as 23.28% \pm 0.04%. This percentage of copper(II) corresponds to a copper(II)-mesityl oxide ratio of 1:2. Only trace amounts of perchlorate ion was present.

On allowing the white solid to be exposed to the atmosphere the white crystals change to a greenish-blue hygroscopic substance, which is only slightly soluble in acetonitrile, presumably indicating partial hydrolysis. When acetonitrile solutions of the blue substance are heated the blue material

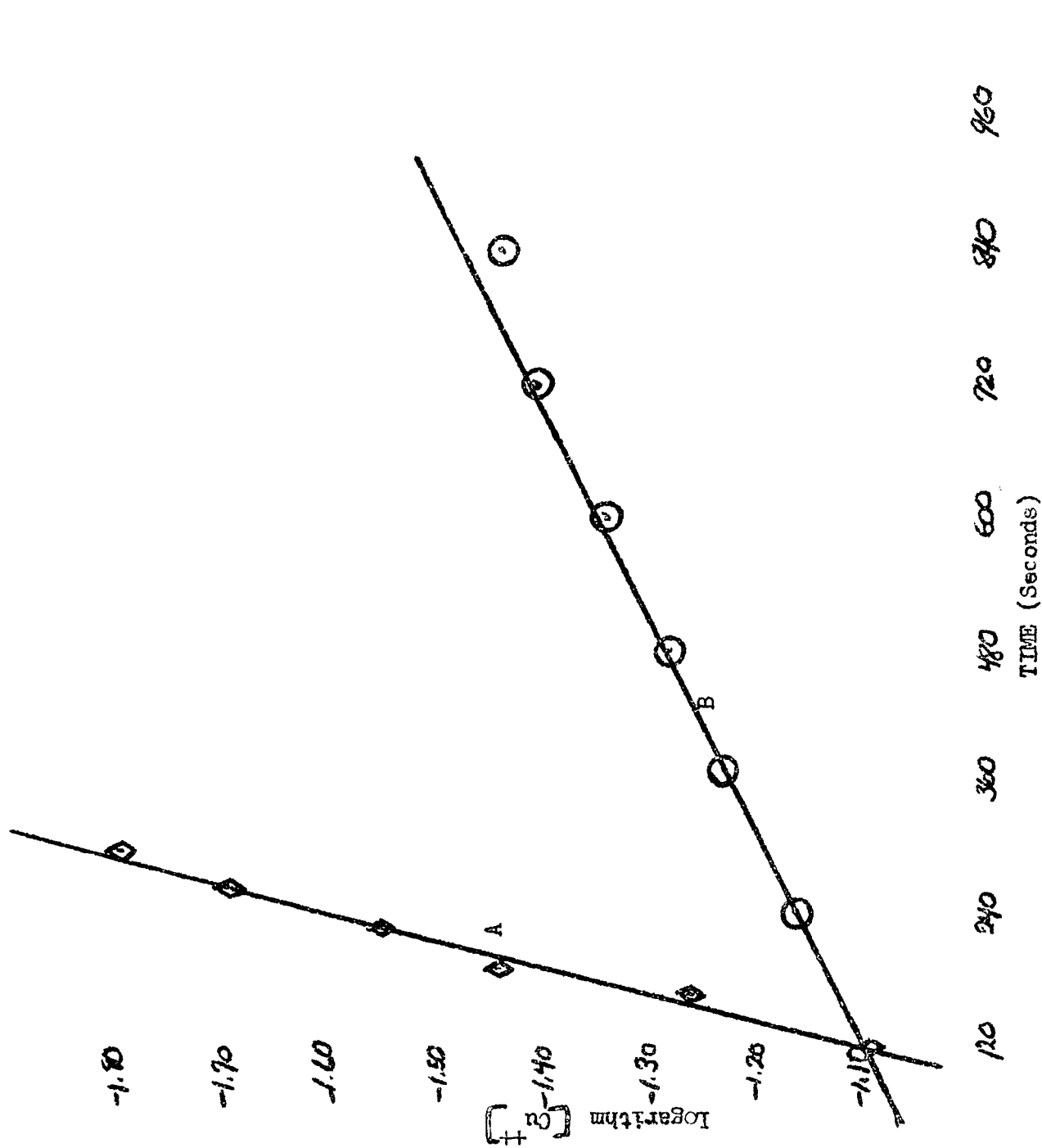


Figure 3--Plots of logarithm concentration of copper(II) ion versus time for solutions of copper(II)-mesityl oxide in acetonitrile at 23 °C. A. $[Mesityl\ Oxide] / [Cu(II)]$ is 66/1; B. $[Mesityl\ oxide] / [Cu(II)]$ is 19/1.

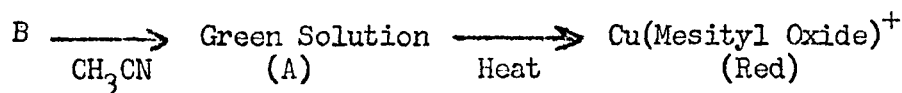
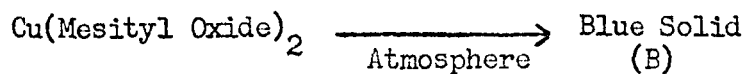
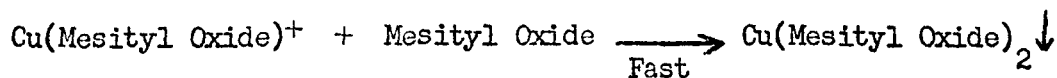
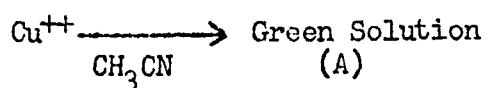
dissolves giving a green solution, which gives the familiar red solution on further heating. The solution returns to its original green color when it is allowed to cool.

Effect of Solvents. -- Using the same experimental conditions, attempts were made to study the reaction of copper(II) with mesityl oxide in other solvents such as dimethylsulfoxide, methanol, and dioxane. Upon addition of mesityl oxide to solutions of copper(II) ion in dimethylsulfoxide a green color slowly increases in intensity. Allowing the mixture to set for about six days resulted only in a very dark green solution, with no spectral indication of the appearance of the red complex nor visual appearance of the white crystalline solid. When mesityl oxide was added to methanolic solutions of copper(II) ion a green color increases in intensity and subsequently changes to a brownish-red color after a period of approximately two days. Only a few white crystals are observed. The reaction in methanol may be speeded up however, by heating. Dioxane solutions of copper(II)-mesityl oxide react in the same manner as acetonitrile solutions of copper(II)-mesityl oxide, but at a much faster rate. The appearance of the red complex and white crystalline solid is almost instantaneous.

Effect of Salts. --0.1 M acetonitrile solutions of anhydrous lithium perchlorate containing 0.02 M copper(II) perchlorate were treated with varying amounts of mesityl oxide. No red complex, nor white crystalline solid was observed. Only when high concentrations of copper(II) and mesityl oxide are used or when solutions were heated did the red color form. No indication of a white precipitate was observed.

Discussion

The results of this study indicate the following reaction scheme for the reaction of copper(II) with mesityl oxide in acetonitrile.



Further analysis of the results indicates that the reaction proceeds at a faster rate in solvents of low dielectric constant. The data also suggests that the copper(II) species being reduced in pure mesityl oxide is the $\text{Cu(Mesityl Oxide)}^+$ ion.

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